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Development of Polymer Phase Change Material for Heat Storage Application

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Abstract

Polymer Phase change materials (PCM's) are the materials which can be used to store the thermal energy for a broad range of applications. The unlike conventional storage materials phase change materials may absorbs or release heat at a constant temperature. They store 6– 12 times more amount of heat per unit volume than sensible storage materials. Increasing demand in solar applications and spacecraft thermal control applications requires continuous development of phase change materials to improve its effectiveness and reliability. The energy storage devices, which are as important as to developing the new sources of energy. In this paper, we can show the combination of low molecular weight polyester resin and Calcium Chloride hexa hydrate (CaCl2.6 H2O) is an inorganic PCM that can be used as PCM's of this study. Differential Scanning Calorimeter (DSC) is an instrument which can be used to measure the thermal characteristics of the phase change materials, Melt Flow Index test were used to characterizing the new developed Compound for storing the heat energy. In this project, the target was to reduce the melting point hence that we could obtain more heat storage for energy saving applications.

Keywords: *Phase change material, latent heat storage, calcium chloride hexahydrate, polyester resin, differential scanning calorimeter*

INTRODUCTION

Thermal energy storage is one of the technologies offer exciting opportunity to improve the efficient and reliable of energy markets. Customers and suppliers of the energy systems will benefit from understanding and using energy storage methods. The latent heat of fusion of solid and liquid phase of heat of fusion to absorb and release the heating or cooling during conversion of phase [1, 2].

PCMs are mainly used in latent heat thermal storage systems for buildings, micro encapsulation, solar systems, composites etc. The applications in wall and floor boards to store heat to provide comfortable temperature to the room [3] .The storage of heat energy in correct forms which can conventionally to be converted into the required form. Energy storage not only decreases the difference between supply and demand and also increases the performance and reliability of energy storage systems and plays an important role in energy conservation [4, 5]. The phase change material can melt and solidify at certain range of temperature, making them effectively in a number of applications. In this project we have analyzed, the non commercial PCMs hybrid composite of low molecular weight materials contains low molecular weight polyester, Methyl ethyl ketone peroxide (MEKP) and acetyl acetone peroxide (AAP) solutions were used as initiators. The development of such material with low freezing and melting point and the latent heat of fusion will leads to break through in formation of hybrid composites during phase conversion.

The increase in fuel prices is the main driving forces are effectively using many non conventional energy sources. This is the one of the part to save the energy. Developing polymer phase change materials for thermal storage applications is the today's exciting research. This is more benefits to humans and also for energy conservation.

The efforts that are being carried out to a greater use of solar energy have been accompanied by the development of thermal energy storage systems in order to surpass the problem of the mismatch between energy demand and supply. In this context latent heat thermal energy storage (LHTES) systems have received a great deal of attention in the last years. Low energy buildings and water heating are important application areas of such systems. Phase Change Materials (PCMs) which are the core of LHTS systems are currently an area of investigation of increasing interest. Latent heat storage by solid-liquid phase transition is a particularly attractive technique, since it provides a high energy storage density and has the capacity to store energy as latent heat of fusion at a constant temperature corresponding to the phase transition temperature of the phase change materials [1]. Several substances, differing in physical and chemical characteristics as well as in thermal behavior have been studied as potential PCMs [1–3]. In order to meet the requisites of particular systems, auxiliary materials are often used with specific functions such as encapsulation or shape stabilizers. Polymeric materials have been proposed to perform different functions in PCMs. Actually polymers appear as promising materials in this context. Besides being possible to choose among a diversity of chemical natures, they can be cross linked and characteristics such as molecular weight, crystalline structure and free volume can be designed in order to meet specific requirements. In this bibliographic survey we look at the application of polymeric materials as PCMs or as auxiliary materials aiming at relating their particular function with their physical, chemical and thermal characteristics.

MATERIALS AND EXPERIMENTS

The unsaturated polyester is one of the thermoset material used in composites for the fabrication of molding compounds with good mechanical properties. The PCMs used in this study is Calcium Chloride hexahydrate which have excellent properties and the melting point of 29˚C. The unsaturated polyester could be mixed with Calcium Chloride hexahydrate. The cross linking reaction between polyester resin and Calcium Chloride hexahydrate allows one polymer chain to connect with other and to produce a three dimensional structure, which convert the resin from a viscous phase. The Calcium Chloride hexahydrate acts as a cross linking agent and viscosity reducer hence the polyester can be processed. The resulting material becomes good mechanical, physical and chemical properties. The curing reaction is more complicated process that is affected due to weather, humidity, uniformity, equipment condition and various factors.

Low molecular weight of pure polyester resin and calcium chloride hexahydrate with density (0.xxxx) g/cm3 was obtained from BORNEO INDAH SDN BHD with the properties such as appearance (white), density (1.12) g/cm3, and stability in the dark below 30ºC. The unsaturated polyester resin contains 50% calcium chloride hexahydrate was prepared by adding 10g of styrene to 100 g from unsaturated polyester resin.(80%up + 20%st).

A various combinations of initiators were used to cure an unsaturated polyester resin. The compressive properties and the curing behavior of the polyester resins in the presence of Vinyl Ester resin were investigated. The results shows that maximize the cure temperature and vinyl ester content lead to improvement in the compression strength and Young's modulus. The unsaturated polyester resin properties were dependent on calcium chloride hexahydrate content including the thermal stability and mechanical properties of the polyester resin reflect the extension of phase segregation. Gel time and peak temperatures were studied in terms of wt% of MEKP, accelerator, filler and glass fibers. They found that the gel time improved with quantity of filler and glass fiber while reduced with amount of catalyst and accelerator. This paper exhibits the thermal properties of the polyester resin containing different concentrations of calcium chloride hexahydrate via measuring viscosity, gel time, maximum temperature and mechanical properties. In addition, the curing reaction process of polyester resin by adding different weight fraction of calcium chloride hexahydrate. This is a very important stage in processing of polyester resin for producing a composite product with high quality and reliability.

Curing Agents

Methyl ethyl ketone Peroxide (MEKP) is used as catalyst and Dimethyl Aniline (DMA) acts as accelerator were obtained from the same supplier for polyester resin. The properties of DMA were as follows: the density at 21–25ºC temperature-(0.944– 0.959) g/cm3, molecular weight-122.28 g/mol, and the chemical symbols-$C_8H_{12}N$.

Differential Scanning Calorimeter

The differential scanning calorimeter was carried out in a TA Instruments DSC 2961, which can calculates the heat flow rate to and from the specimen with respect to the temperature and time, sample weight of 6– 12 mg at heating rate of 10ºC/min. There is a reference material introduced in this method to compare the rate of heat exchange irrespective of whether it is an exothermic such as melting property, crystallization and curing of mixtures with respect to temperature. Change in heat capacity is also found using this test. The testing temperature is usually ranges from 150–200˚C.

Mould Design and Fabrication

Specimens have been prepared for four different salt hydrate PCM content 1%, 2%, 3% and 5% concentrations with pure polyester resin. The accelerator and catalyst were added 1, 2, 3 and 4% by volume of 100 ml of polyester resin, mixing with mechanical stirrer for 20–30 minutes and laid up in the mould for 24 hours. The mould should be well cleaned and dry, for this reason, a release agent (wax) is laid up on the mould before powering mixture. The same process is applied to prepare the resin specimens with fixed MEKP concentration of 1% and change the DMA volume fraction stared from 1%, 2%, 3% and 4% by volume of pure polyester resin. The mould consists of three parts, the base part and the upper part made form glass plate while the intermediate gasket made from foam board with 3 mm thickness.

RESULTS AND DISCUSSIONS

Measurement of Viscosity

LVDV-II+Pro Viscometer were used to measure the viscosity of the polyester resin for different calcium chloride hexahydrate weight concentrations at different temperatures. A standard glass beaker with 500 ml was used in this test. The experiments are start at 31ºC and raise until 60ºC.

As expected with rise of temperature the viscosity may drops significantly. It has been found that the viscosity decreases with increase of calcium chloride hexahydrate concentration ratio, the results shows that the viscosity was 215.3 cP at 31 ºC and 62.5cP at 60ºC and the percentage decreasing was 28.56% for the first ratio of (80% polyester +20% Cacl2.6H2O), while the percentage decreasing for the ratio of (70% polyester +30% Cacl2.6H2O) is 64.83% and for the last calcium chloride hexahydrate ratio of (60% polyester +40% Cacl2.6H2O) is 61.59%.

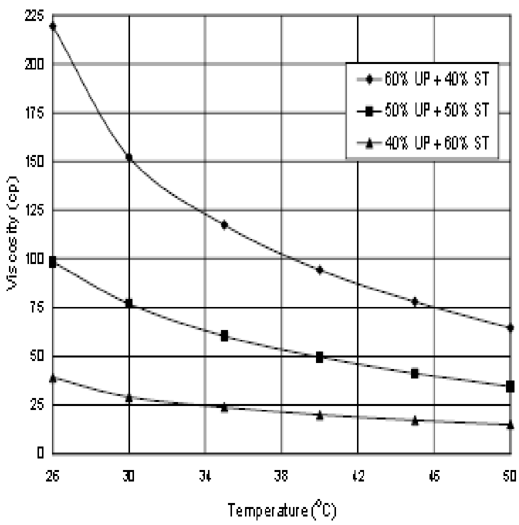

Fig. 1: Viscosity Change with Temperature Polyester Resin Containing Different Concentrations of PCM.

Density Measurement

The calcium chloride hexahydrate ratio controls the reactivity of the pure polyester resin and also the cross linking density of the final result. The density variations with the increase in calcium chloride hexahydrate concentration at 29ºC. It is found that the density of the polymer matrix is decreasing while the calcium chloride hexahydrate ratio was

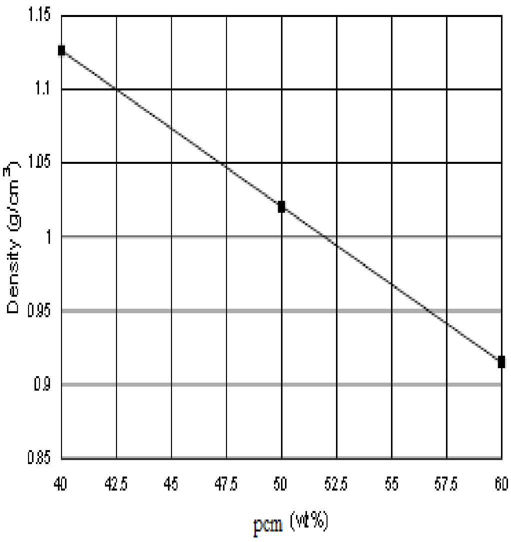

Fig. 2: *Density Change with PCM Concentration Ratio for Unsaturated Polyester Resin.*

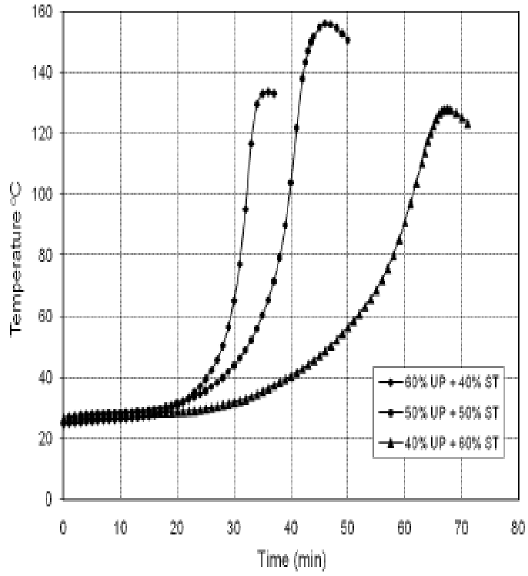

Fig. 3: *Curing Time for Different Volume Fraction of Unsaturated Polyester Resin with 1% MEKP.*

Cure Characteristics

Curing Time and Peak Exothermic Temperature

The cross linking reaction in the processing of unsaturated polyester resin into a composite product, also does the exothermic temperature of cure after end of the processing. The cross linking reaction is a high exothermic reaction, and the temperature can rise up to 110–220ºC. The maximum exothermic temperature was about 160ºC for the ratio 80% of calcium chloride hexahydrate followed 20% at about 140ºC and 30% at about 125ºC.

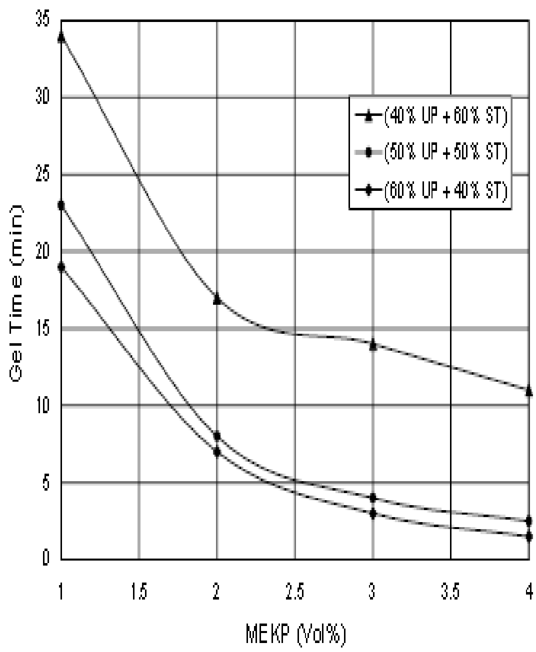

Fig. 4: *Gel Time for Unsaturated Polyester Resin Containing Different Concentrations of PCM and MEKP Ratios.*

DSC Results for Different Weight Concentrations of PCM

The output of a DSC measurement is a plot of the difference of heat delivered to the sample and to the reference as a function of the sample temperature for (80% polyester-20% pcm) polyester resin with 1%MEKP. The figure shows that the significant changes in TG of unsaturated polyester resin for different weight concentrations of pcm with different MEKP and DMA concentration ratios. In the first ratio of pcm 20% there insignificant changes with increasing MEKP, while Tg reduces with adding 0.1vol% DMA then started to increases with the increasing of DMA. While for the second ratio of pcm the maximum transition temperature is at 2vol% of MEKP and after that stared to decrease with increasing of MEKP. The glass transition temperature has the equal trend for DMA and the maximum is at 0.2 vol%. It is found that Tg measured by DSC increases as the MEKP level increases for certain level and then decreases.

The Effect of Moisture Content

The effect of varying the level of water content on the exothermic behavior of the unsaturated polyester resin for 80% calcium chloride hexahydrate as shown in Figure. The reaction of water with unsaturated polyester resin the rate of temperature increases is almost equal, but gel time gets increased. Because of the water slows the reaction by absorbing the heat from the storage system. Gel time was 40min for the 0% water, 43 min for the 1 vol% water and 46 min for the 2 vol% water. However, when the concentration of water was 3 vol% water the gel time has decreased and reached 34 min (2 min) only above the 0% water ratio. That means after the 3% water concentration ratio there was no action affecting the gel time. Otherwise, it may affect the mechanical and chemical properties. In addition, the water affected the action of initiator and accelerator system. Water Bubbles may appear in the polyester resin because the water can increase reactivity in some peroxide system.

Mechanical Properties

Tensile Test

The tensile test was performed in accordance to ASTM (D638) specification. Four dumbbell shape (Type I) specimens from each matrix were tested in Universal Testing Machine (UTM), with load cell of 50 KN. The specimen was loaded in tension at a speed of 6.5 mm/min. An extensometer of 8 mm gage

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length was mounted on the specimen for measurement of the strain. The cross section area of specimen was determined using a digital micrometer. The average results from four specimens were taken.

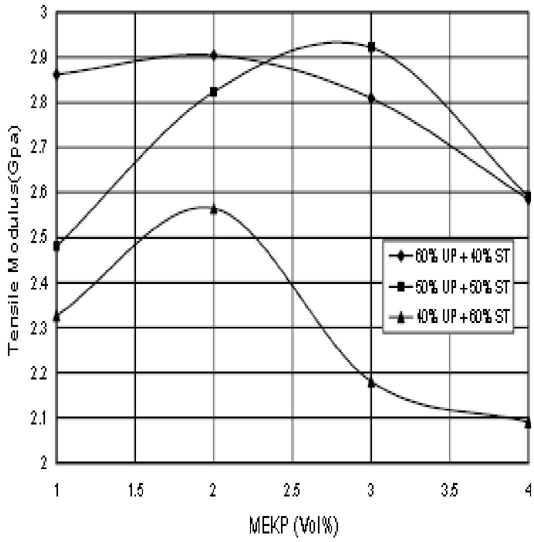

Fig. 5: *Effect of PCM Concentration Ratio on Modulus for Unsaturated Polyester Resin.*

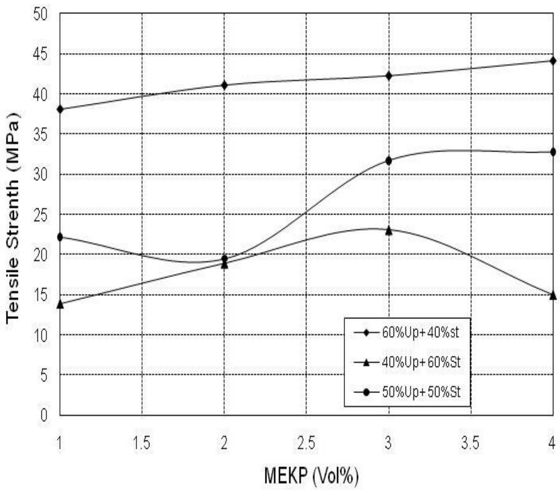

Fig. 6: *Effect of PCM Concentration Ratio on Maximum Strength for Unsaturated Polyester Resin with Different MEKP Concentration.*

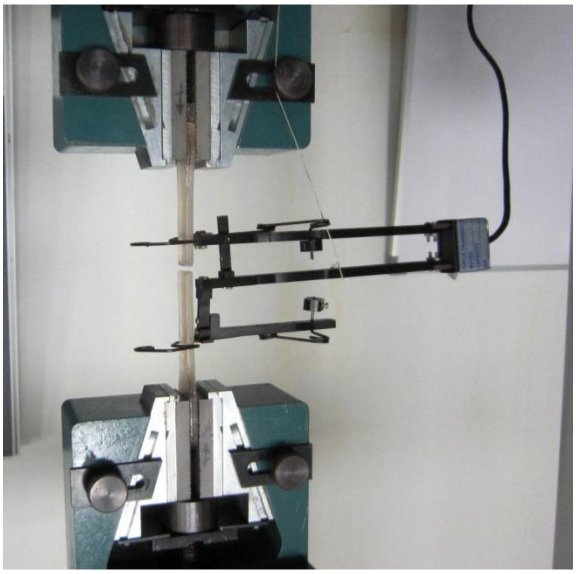

Fig. 7: *Tensile Test T-Machine Setup.*

The Effect of MEKP and PCM Concentrations on Tensile Strength

The results of mechanical properties for the polyester resin were determined. The results of the effect of MEKP concentration on the tensile strength of cured samples at a fixed (80%up + 20%pcm). It can be found that the load increases to the maximum value and then suddenly decline as a brittle fracture was placed in the material. The tensile strength does not significantly change with the rising of MEKP ratio. In fact, the percentage of increase between the strength for 5% MEKP and the other ratio is less than 10% while the other ratios are (1, 2, 3) % about (2–3) %. The mechanical properties of the cured samples are varied from soft to hard, depending on the molar mass of the end grouping. A high

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molecular mass will give more hardness, tensile and flexural strength of the final cured material. If the molecular mass is low, the mechanical properties of the cured resin will be less. Calcium chloride hexahydrate will generally more brittleness to the specimen, therefore, the embrittlement causes reducing the internal stresses in the part because of the increase of part shrinkage that occur with higher degrees of cross linking. In another expression the tensile strength increases with decreasing of PCM weight concentration ratio at constant MEKP concentration.

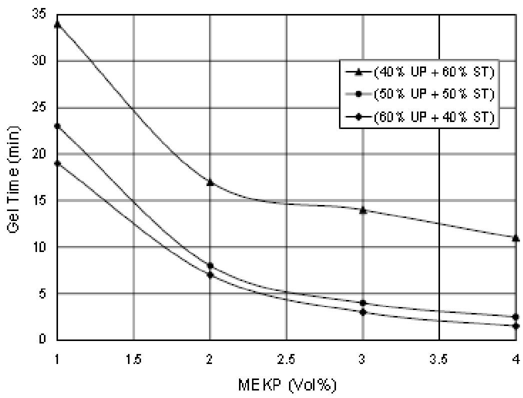

Fig. 8: *Gel Time for Unsaturated Polyester Resin Containing Different Concentrations of PCM and MEKP Ratios.*

CONCLUSION

1. The conducted project has revealed the following:
2. The physical parameters such as viscosity and density are decreases with the increase of environmental temperature and different weight concentration of PCMs used.
3. The PCM ratio controls the reactivity of the unsaturated polyester resin and also the cross linking density of the final network structure by increasing the gel time, time to peak, and exothermic temperature.
4. Maximum strength and modulus of elasticity have the same trend for different weight concentration ratios of PCM and for certain concentration of polyester resin, different ratio MEKP and DMA have a significant effect on the maximum tensile strength, while DMA has insignificant effect young's modulus.
5. The presence of polymer matrix is usually inanimate the cross linking reactions, by added mass which is absorb the heat that occurs and delaying the gel time interval.
6. The moisture content in the resin affected the curing reaction by increase of the gel time and time to peak, while there insignificant effect on the exothermic temperature for the equal MEKP concentration at an operating temperature.
7. The glass transition temperature TG decreases with increase of calcium chloride hexahydrate concentration for

1 vol% MEKP, beyond that there is insignificant effect on TG with the increasing of MEKP and DMA.

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